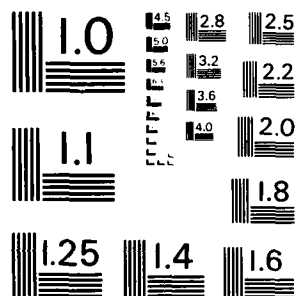


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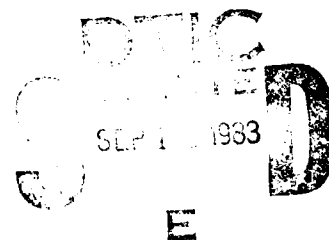
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THE 1982 INTERNATIONAL CONGRESS OF PHOTOGRAPHIC SCIENCE

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Univ. of North Carolina, Chapel Hill

26 June 1983



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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER C-9-83	2. GOVT ACCESSION NO. AD-A13 2372	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) The 1982 International Congress of Photographic Science		5. TYPE OF REPORT & PERIOD COVERED Conference
7. AUTHOR(s) Lawrence Slifkin Univ. of North Carolina, Chapel Hill		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Office of Naval Research, Branch Office London Box 39 FPO N.Y. 09510		8. CONTRACT OR GRANT NUMBER(s)
11. CONTROLLING OFFICE NAME AND ADDRESS		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE 26 June 1983
		13. NUMBER OF PAGES 6
		15. SECURITY CLASS. (of this report)
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) APPROVED FOR PUBLIC RELEASE: DISTRIBUTION UNLIMITED		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Photographic science Chemistry of crystalline solids Physics of crystalline solids		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Conference papers treated topics ranging from fundamental solid state physics of the silver halides to problems in the production of photographic products. This report describes primarily contributions closer to the chemistry and physics of crystalline solids.		

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THE 1982 INTERNATIONAL CONGRESS OF
PHOTOGRAPHIC SCIENCE

The latest International Congress of Photographic Science met at Cambridge Univ. (UK) from 6 through 10 September 1982. As in Rochester, NY, in 1978, there were about 150 papers ranging from fundamental solid state physics of the silver halides to problems in the production of photographic products. This report primarily describes contributions closer to the chemistry and physics of crystalline solids.

The first papers dealt with ionic properties of crystals of AgCl and AgBr, the diffusion of ions, and the subsurface ionic space charge. The migration of cations in AgX was reviewed by A. Lasker (Clemson Univ., SC), who stressed that our understanding of these substances is better than for any other ionic materials. He pointed to the discovery and measurements of the temperature dependence of the formation enthalpies of the lattice defects, to the demonstration of the effect of d-shell occupancy on the solute activation energy, to the effect of ionic mismatch, and to the elucidation of the details of impurity ion-vacancy association.

One example of such research was provided by N. Bannon, J. Corish (Univ. College, Dublin), and P. Jacobs (Univ. of Western Ontario), who presented calculations of the temperature dependence of the formation and migration enthalpies for both self- and impurity-diffusion; the results are consistent with the experimental observations that the Arrhenius plot is linear in some cases but is definitely curved in others. One such experimental determination is that of the diffusion

of K^+ in AgX, described by P. Cardenga and A. Laskar (Clemson); in both AgCl and AgBr, the Arrhenius plots definitely curve upward, reflecting the fact that the Gibbs free energy of Frenkel defect formation decreases faster than linearly with increasing temperature.

The subsurface ionic space charge phenomenon was reviewed by L. Slifkin (Univ. of North Carolina). This effect arises because a difference between the formation-free energies of the two components of the Frenkel pair leaves a net excess of negatively charged jogs on the surface. As a result, there is a substantial potential difference (about 0.2 V) across a screening depth of several hundred angstroms, and this causes large perturbation of all the defect-related phenomena (including the photographic process).

Y. Tan (Kodak) reported the effects of several photographically interesting adsorbates on the surface potential of AgBr crystals. He found adsorption of Au, Ag_2S , or excess Ag^+ (from aqueous solution) each caused the surface to be less negative (relative to the interior) by amounts on the order of 0.1 V. A calculation of the effect of external solution pAg on the surface potential of microcrystals (as used in photographic emulsions) was reported by L. Ketellapper (Agfa-Gevaert, Mortsel, Belgium), F. Gallens, and W. Maenhout-Van der Vorst (Gent). The space charge in AgI was studied by N. Starbov and J. Malinowski (Bulgarian Acad. Sci.) by monitoring the longitudinal ionic conductance of evaporated thin-film crystals as a function of thickness and of doping. They demonstrated that AgI, as earlier found for AgCl and AgBr, does indeed have a subsurface space charge that is enriched in interstitial Ag^+ ions.

The physics of photocarrier trapping in the silver halides was introduced in a review paper by H. Kanzaki (Tokyo). He summarized his group's recent work on localized electrons and holes at very low temperatures; the researchers used techniques such as transient optical absorption, modulation of luminescence and electronic conductivity, and halogen desorption. He argued that the low-temperature, shallow electron trap is the interstitial Ag^+ , produced by the optical irradiation, and that photoholes can be

trapped by cation vacancies, with a trap depth of about 0.5 eV. It is not understood, however, why such a center has not been seen by electron paramagnetic resonance (EPR) spectroscopy. In contrast to such experiments on single crystals, P. Hada, M. Kawasaki, and H. Fujimoto (Kyoto) measured the lifetime of single silver atoms formed in a photographic emulsion at room temperature by exposure to a series of flashes. From a determination of the dependence on interflash interval of the efficiency of formation of a photographic latent image, they obtained a lifetime of 1.1 seconds at 20°C, with an activation energy of 0.76 eV. The Ag^0 is on the surface of the emulsion grain, and its stability is a function of the ambient atmosphere; thus, evacuation produced an increase in lifetime to 300 seconds. R. Grinter, G. Morris (Univ. of East Anglia, UK), and M. Harding (Ilford, Ltd., UK) proposed that trapped carriers such as Ag^0 might well be studied profitably by magnetic circular dichroism (MCD). As a start on such a project, they have already looked at the MCD spectra of AgCl and AgBr with no deliberately added Ag^0 centers, and they found intrinsic spectra with features that are still unexplained.

Two papers on the EPR study of the trapping of photocarriers in the NaCl-AgCl mixed-crystal system were contributed by Th. Mussig and F. Granzner (Frankfurt) and by M. Symons and M. Olm (Leicester). In specimens with a very low proportion of AgCl, the Ag^+ acts primarily as an electron trap, but if the concentration of AgCl is somewhat larger, the Ag^+ functions as a hole trap. In addition, if specimens in the mid-range are aged to promote phase separation, irradiation then produces a long-lived conduction electron resonance, apparently arising from photoelectrons confined to the phase interface regions. Another method used to study photocarrier trapping is measurement of photoconductivity, often using low-temperature microwave absorption techniques in the case of photo-

graphic emulsions. A report by F. Callens and W. Maenhout-Van der Vorst (Gent) showed that in such an experiment the sample must be cooled slowly, otherwise a nonequilibrium distribution of defects is quenched in. The authors discussed the phenomenon in terms of frozen-in interstitials, but another possibility is a nonequilibrium degree of association between vacancies and solute ions. One further experiment on the deep electron trapping in a AgBr:I photographic emulsion was described by T. Harada, H. Ohtani, J. Suzuki, and T. Koitabashi (Konishiroku Photo Ind.). After a pulsed exposure to light, detrapping was monitored by observing the electronic conductivity (in a microwave cavity) as the temperature was increased; the researchers found two distinct trap populations 0.22 and 0.30 eV deep.

One of the reasons the photographic scientist is interested in photocarrier trapping is that it is a critical aspect of the formation of the latent image. J. Hamilton (Kodak) reviewed an analytical model of the kinetics of the various trapping and detrapping processes in an irradiated photographic grain. By requiring that no center ever acquire a charge greater than one electronic charge, and by demanding that the results on latent image formation fit various significant photographic phenomena (e.g., reciprocity failure, effects of sensitization), he could come to a number of interesting conclusions. He argued that an unsensitized microcrystal contains many shallow traps for photocarriers, but no deep traps; that the precursor of the latent image speck has equal cross section for trapping of a hole and an electron, and hence must be located at a jog (so that the charge is always either plus or minus one half); and that the main source of inefficiency in the process is the recombination of free electrons with trapped holes.

Two papers describing Monte Carlo simulations based on the above model of the photographic process were given by P. Xia (Chinese Acad. Sci.) and by N.

and J. Malinowski (Bulgarian Acad. Sci.). Xia expanded the Hamilton model by envisaging the product of sulfur sensitization acting as a trap for either a hole or an electron. N. and J. Malinowski modified the Hamilton treatment of the fate of the photohole by including trapping at cation vacancies and by proposing that the holes are finally eliminated by a second-order production of Br_2 molecules at the surface. Experimental data in support of such ideas were reviewed by J. Malinowski, who also argued that Frenkel defects could be produced by the trapping of a hole at a jog.

Quite a different model of latent image formation was described by J. Mitchell (Virginia), who was largely concerned with the mechanism of concentrating the effects of absorption of several photons into one, or a few, specks of silver per grain. He argued that the sensitized emulsion contains Ag_2 clusters, which can be dissociated upon absorption of a hole or can grow upon absorption of an electron. If local coulombic forces at positively charged centers can result in the production of Ag_1^+ , Mitchell concluded that a latent image speck can be formed as the result of a single effective photon event.

One question that arises in connection with the theory of the concentration mechanism is whether silver atoms can migrate along the surface of the AgX grain, either as neutral atoms or by first ionizing. A. Panov and J. Malinowski (Bulgarian Acad. Sci.) attempted to test the possibility by looking for an effect of a transverse electric field on the image created by evaporation of silver atoms through a slit onto an AgBr surface; no effect was observed, but it is possible that the resolution will have to be improved to obtain a definitive result. Such a result would be relevant to a model of latent image formation presented by H. Shalitt (Rochester Inst. Tech.), who emphasized the role of elastic inter-

actions among defects and proposed that the neutral silver atom also exists within and migrates within the interior of the grain. V. Zhelev (Bulgarian Acad. Sci.) demonstrated that silver does indeed migrate (in some form) away from clusters (probably by ionization and migration of Ag_1^+). Zhelev studied the effect of performing a sulfur-sensitization after, rather than before, exposure of a AgBr layer to light. The results of selective development of the surface and internal latent images showed that stable clusters of silver in the interior could be induced to "evaporate" and reappear on the surface after the production of deep surface traps by sulfur-sensitization.

Further work on redistribution of surface silver was described by S. Fujiwara (Kyoto). He studied the effects of exposing photographic emulsions to successive flashes, with variable aging times between flashes and before development, to obtain information on the stability of pre-latent image specks and the effects of surface migration of silver. An interesting experiment on electronic effects in determining latent image distribution in inhomogeneous systems was reported by V. Platikanova (Bulgarian Acad. Sci.). She prepared evaporated films of AgBr:I , which were then covered with a thin (150 angstrom) epitaxial layer of AgCl ; this increased the photographic sensitivity substantially. It was possible to show that the photoelectrons were created primarily in the underlying AgBr but migrated into the AgCl overcoat to form the latent image specks.

The addition of group VIII cations can produce large effects on the photographic properties of a silver halide emulsion; six papers by scientists at Eastman Kodak focused on the properties of the Ir^{3+} ion in single crystals and in emulsions of AgBr . Many techniques were used, including luminescence, optical absorption, Raman spectroscopy, EPR, photoconductivity, spectral sensitization measurements, and

development studies. It is clear that the Ir^{3+} is a potent trap for photoelectrons, with a trap depth of 0.4 eV. Moreover, the latent image specks apparently form at the sites of the iridium ions. It was suggested that after electron capture the resulting Ir^{2+} loses one of its charge-compensating cation vacancies, followed by an ionic relaxation and electron transfer to produce the original Ir^{3+} , compensated by two vacancies, plus an atom of neutral silver. Repetition of the cycle would result in the formation of a latent image speck.

Several papers dealt with effects of other cations. T. Yan and J. Yue (Hefei, China) showed that incorporation of 10^{-4} mole fraction of Cd^{2+} significantly increased the photographic speed of a set of $\text{AgBr}:\text{I}$ emulsions, an effect they attributed to an influence on the growth habit of the microcrystals. On the other hand, C. Rippon and B. Levy (Polaroid) found that treatment of their AgBr emulsion with aqueous CdCl_2 caused a decrease in ionic conductivity by a factor of several hundred and significantly decreased the rate of decay of the Dember photovoltage. They interpreted their kinetics data in terms of the production of Frenkel defects by irradiation and the subsequent trapping of the photoholes at the cation vacancies; they could thereby also account for the increase in photographic speed that results from incorporation of Cd^{2+} . The effect of Pb^{2+} adsorbed onto the surfaces of AgBr emulsion grains was reported by L. Ketellapper, A. De Rouck (Agfa-Gevaert), F. Callens, and W. Maenhout-Van der Vorst (Gent); the resulting decrease in photographic speed and in electron lifetime, and the shift in luminescence could be understood in terms of the introduction of electron traps by the Pb^{2+} .

The role of chemical sensitizers (and the questions yet unanswered) was

the subject of a review by H. Spencer (Kodak). Sulfur sensitization produces aggregates of Ag_2S on the surfaces

of the microcrystals; the aggregates act as electron traps and are the sites of the latent image formation. Sulfur-gold sensitization provides yet a deeper trap and imparts a greater stability to the growing silver speck. Reduction sensitization produces neutral silver on the surface, which acts as hole traps rather than as sites for latent image formation, presumably because the atoms or clusters are not at positively charged jogs. Spencer pointed out that an optimally sensitized emulsion, including treatment by hydrogen (to remove latent image oxidants), produces grains that require absorption of only three photons each to become developable. As an example of the complexity of such effects, H. Rollar and K. Hoffman (Agfa-Gevaert) showed that whereas the photoelectron lifetime decreases monotonically with increasing digestion in a sulfur-sensitizing bath, the photographic speed goes through a maximum, indicating the presence of at least two different effects (e.g., presence of multiple, competing sensitivity sites after long digestion times). The effect of sulfur sensitization on the photo-induced EPR signal of an adsorbed dye layer was shown by C. Chen and T. Liu (Chinese Acad. Sci.) to depend on whether the emulsion had a preponderance of electron traps or hole traps before sensitization--the Ag_2S

apparently can function as a trap for whichever type of photocarrier is still left. P. Faelens (Agfa-Gevaert) discussed the phenomenon of high-intensity reciprocity failure and showed how analysis of the effects of various treatments could give information about the mechanisms of sensitization, the relative efficiencies of different types of trap, and the growth of the latent image.

The many-faceted influences of the gelatin of a photographic emulsion were surveyed by W. Berg (ETH-Zurich). It not only provides a convenient support medium but, among other things,

(1) allows free growth of isolated microcrystals during precipitation, (2) influences adsorption and sensitization by other additives, (3) provides some sensitization itself, (4) enhances developability of the latent image, and (5) most important, stabilizes the latent image speck against oxidation during the period between exposure and development. Further experiments on the mechanism of the latter effect were described by A. Herz (Kodak), who also reviewed what is known about the effects of many other chemicals that are added to photographic emulsions to influence Ostwald ripening, recrystallization, development, stability of sensitization, and production of fog centers. The effects of some of the additives on the ionic conductivity (measured by means of dielectric loss) were cited by B. Peng, Y. Peng, X. Wu, and Z. Li (Chinese Acad. Sci.). Adsorption of photographic stabilizers (Ag^+ complexers) caused a hundred-fold decrease, as did other Ag^+ -complexing ions to a smaller extent, but there was no effect on the ionic conductivity of sensitization with S, Au, or by reduction.

E. Moisar (Agfa-Gevaert) discussed the different morphologies of microcrystals that result from different precipitation schemes and how they influence the photographic properties. He pointed out the qualitative differences between (111) and (100) surfaces, the effects of pairs of (111) twin planes, the results of carrying out the precipitation so that mixed halide composition varies with radius (i.e., an iodide-rich core to increase speed for formation of internal image), and the effects of varying the pAg. P. Broadhead and G. Farnell (Kodak-Harrow) gave data on the variation with grain size of photographic speed and quantum efficiency in a set of sensitized $\text{AgBr}:\text{I}$ emulsions. The photographic speed increases with larger grain sizes up to about $6 \mu\text{m}^2$; the quantum efficiency is small for both very small and very large grains. (Apparently very small grains do not undergo sensi-

tization--for unknown reasons--and very large grains form a dispersed image.)

In what this observer considered the most interesting presentation at the congress, P. Gilman (Kodak) discussed the phenomena of spectral sensitization and desensitization by adsorbed layers of dye. He showed how the range of dyes that will act as sensitizers can be greatly extended if the growing image speck is protected against oxidation. One can achieve this by removing water and oxygen, by assuring the presence of excess Ag^+ in the external medium, or by doping with Ir^{3+} , which forms internal image with great efficiency. He pointed out that for dyes in which the energy of the excited electron is below the silver halide conduction band, one can still produce image, either by thermal excitation into the conduction band or by production of surface silver atoms without band injection.

T. Tani (Fuji Photo) studied the thermal activation requirement for a series of dyes over the temperature range -100°C to room temperature. The sensitization and desensitization properties were correlated with the effective activation energy; the latter is presumably made up of several components but largely involves the transfer of a hole from the excited dye to the underlying AgX grain, in the case of desensitizing dyes. The temperature dependence for the transfer of a photoelectron, in the case of a sensitizing dye, was studied by R. Hailstone (Kodak). He found that the effective activation energy correlated with the energy level of the excited dye, but he had to assume that the photoelectron is stored in an intermediate state if quantitative fitting of the data were to be obtained.

S.-T. Lee (Kodak) described a quantitative investigation of the energy levels of photographic dyes. Lee used both optical absorption and ultraviolet photoemission to determine the energies of the highest occupied state and the lowest unoccupied level. He found that the spectral sensitization by members of a set of dyes was well correlated with

In the phenomenon of supersensitization, two dyes are present on the surface, and there is a transfer of energy (not electrons) from the poor sensitizer to the good one. A. Muentzer and J. Kittle (Kodak) have examined such effects by measuring the luminescent and the photographic properties of systems in which the amount of coverage of the surface by monomers of the two dyes was varied. The researchers observed the expected energy migration and transfer processes. A related experiment, but this time on a model system of an evaporated silver halide film with adsorbed dye layers of various structures, was reported by R. Steiger (Ciba-Gelgy). The spacings

In addition to the papers summarized in this report, many other contributions dealt with some of the more technical aspects of photographic science. There were also discussions of contemporary advances in electronic image recording and the extent to which it may supplant conventional silver halide processes. The topics are not treated in this report, but one interesting contrast between the two schemes is worth noting. In the case of electronic devices, the scientific understanding leads to application; in silver halide photography, however, scientific knowledge of the microscopic mechanism has still not yet caught up with practical application.

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